Total Mercury Analysis in Aqueous Samples

James P. Hurley
Bureau of Integrated Science Services
Wisconsin Department of Natural Resources

April 1994

Revision 2

Total Mercury Analysis in Aqueous Samples

1.0 Introduction

This manual contains instructions for measuring total mercury in aqueous samples. Both experienced chemists and neophyte technicians will find these protocols understandable and useful. Besides dictating each step in the total mercury analysis, this manual provides explanations, suggestions, precautions, definitions, tips and helpful background information. Although the stepwise protocols are complete, this manual cannot replace a knowledgeable, experienced, and friendly human instructor.

Environmental Mercury Pollution

After new sampling and analytical techniques were developed and applied during the mid 1980s, researchers discovered environmental mercury concentrations were up to 1000 times lower than previously reported. For many years, scientists had unknowingly contaminated their samples during collection and analysis. Scientists now believe the concentration of mercury in our atmosphere, oceans, and lakes is often quite low. In some cases, concentrations are almost too low to measure.

Because mercury is found in paints, batteries, fluorescent lights, electric switches, and many other human inventions, concentrations of the element tend to be quite high inside and near buildings. Unfortunately, the situation is often worse in laboratories which frequently house mercurial reagents and mercury equipped instruments. Mercury's ubiquity, along with some of its chemical properties, make contaminating environmental samples virtually inevitable. For this reason, special techniques must be implemented when analyzing total mercury samples.

2.0 Clean Techniques

The following guidelines were developed to minimize the probability of sample contamination. These Clean techniques should be followed when analyzing mercury samples.

2.1 Never open mercury sample bottles indoors unless working in a trace-metal clean lab.

2.2 Keep sample bottles sealed in plastic bags except when adding to or taking from the bottles.

2.3 Minimize sample contact time with atmosphere. Avoid breathing into samples.

2.4 Wear a lint free suit.

2.5 Wear plastic gloves when handling mercury samples and analytical equipment such as gold traps and bubblers.

2.6 Do not place potentially contaminated objects such as pipettors, balances, and lab benches into contact with mercury sample bottles. Cover equipment and benches with plastic bags, gloves or particle free towels if necessary.

2.7 Work in a laminar flow or HEPA-filtered hood whenever possible.
2.8 Keep lab work areas uncluttered.

2.9 Clean the trace-metal clean lab frequently.

3.0 Definitions

3.1 *Analytical Trap*: This is the gold trap that captures the mercury from a sample trap and subsequently releases that mercury into the analyzer. It is the trap farthest down-stream and is not routinely removed from the analytical system.

3.2 *Analyzer:* The mercury analyzer is a cold vapor atomic fluorescence spectrophotometer (CVAFS). In the CVAFS, light from a small mercury vapor lamp is shined through a quartz flow cell that contains mercury in a stream of argon carrier gas. This light excites the mercury atoms which subsequently emit more light. The amount of light emitted by the mercury is proportional to the amount of mercury passing through the cell. The light emitted by the mercury atoms passes through a filter (254nm) and into a photomultiplier tube (PMT) which converts the light into an electrical signal. This signal is received and plotted by a stripchart recorder or integrator.

3.3 *Blank* (noun): The mercury that is associated with equipment and reagents must be measured; this quantity of mercury must subsequently be subtracted from the mercury measured in samples. This measured quantity of mercury from background levels is called a blank. Sometimes blanks are associated with specific objects, such as a bubbler blank or a BrCl blank. Sometimes blanks are associated with specific processes, such a traveling blank or a digestion blank. The term blank can also be used in a more generic sense to refer to the sum of background contamination from all potential sources.

3.4 *Blank* (verb):

1) The process of measuring the quantity of mercury that is associated with equipment and reagents is called blanking. For example, during an analysis session, the analyst must blank the bubblers.

2) The process of thermally desorbing mercury from a gold trap is called blanking. This is sometimes also referred to as analyzing a trap.

3.5 *Bubbler:* A flask and stopper system used to purge aqueous samples. Typically, 250 mL, flat bottomed, spherical, 24/40 jointed, boiling flasks are used for total mercury analyses.

3.6 *Bubbler Stopper:* This is a modified ground glass joint which fits into the bubbler flask. The stoppers have a glass tube which extends from a vertical gas inlet on the top of the stopper and terminates in a frit near the bottom of the bubbler flask. An outlet extends horizontally near the top of the stopper.

3.7 *Bubbling Matrix*: An aqueous mixture which may contain any combination of deionized water, HCl, $SnCl_2$, BrCl, $NH_2OH{\cdot}HCl$, total mercury standard, and/or water sample. This is the solution out of which elemental mercury is purged.

3.8 *Coil:* Coils are made from nichrome wire. These coils are used to desorb mercury from gold traps. Variable autotransformers are used to apply a potential of approximately 10 VAC to the coils; this heats the gold traps desorbing elemental mercury.

3.9 *FEP:* A type of Teflon (Fluorinated Ethylene-Propylene).

3.10 *Glass Wool:* Fibrous strands of silanized glass. Plugs of glass wool are used to hold soda-lime chips in soda-lime traps.

3.11 *Gold Trap:* Gold traps are made from a 9 cm length of 4 mm I.D. quartz tube. The tubes contain approximately 1 g of gold coated beads held in place with silanized glass wool plugs. A constriction in the quartz tube holds all the packing materials in place. Because elemental mercury forms an amalgam with gold, these gold coated bead traps are used to preconcentrate mercury purged from aqueous samples.

3.12 *Prereduce:* The addition of $NH_2OH \bullet HCl$ to a brominated sample. Chemically reduces excess BrCl which could damage the gold traps.

3.13 *PTFE:* A type of Teflon (Poly Tetra Fluoro Ethylene).

3.14 *Purge:* To pass N_2 bubbles through an aqueous matrix to remove and trap the elemental mercury contained within that matrix.

3.15 *Regulator Units:* These consist of the single or two stage regulators on the N_2 and Ar cylinders and any needle valves and other brass or Teflon fittings connected to these regulators.

3.16 *Sample Traps:* These are the gold traps that are first attached to the purging apparatus to capture elemental mercury and then connected to the analytical system for mercury measurement. These traps are connected to the Tenax TA® pretraps or soda-lime traps during bubbling and to the argon line and analytical trap during blanking.

3.17 *Scrubbing Traps:*These are the gold traps attached to the purging and analytical systems that are intended to remove contaminant mercury from the N_2 and Ar gases.

3.18 *Soda-lime Trap:* Soda-lime traps are made from 10 cm lengths of 0.9 cm I.D. Teflon tubing. These traps are packed with non-indicating, 8-14 mesh, reagent grade soda-lime; the ends are plugged with glass wool. These traps neutralize acid fumes and trap water vapor during the purging process.

3.19 *Tenax TA®:* A porous polymer based on 2,6-diphenyl-p-phylene oxide used to trap matrix-interferents associated with some tributary samples. Placed between the gold trap and soda lime trap.

3.20 *Timer Controller:* A device used to switch coils and fans on and off at appropriate times during gold trap blanking.

3.21 *Total Mercury:* The sum of all the different chemical forms of mercury (includes inorganic and organic forms).

3.22 *Working Standard:* A solution with a known concentration of Hg^{2+}. This solution, mixed form more concentrated primary and secondary standards, is used to calibrate the analyzer. It typically has a concentration of 10 ng/mL.

4.0 Cautions

The following list of warnings and prescriptions is incomplete. Consult the material safety data sheets that are shipped with all hazardous chemicals.

4.1 *BrCl:* Extremely corrosive. Contact with any body part will cause severe injury. The BrCl solution releases toxic and extremely caustic Cl_2, Br, and BrCl fumes which will cause severe damage to the respiratory system if inhaled. Flush affected areas with water and mild soap. Always use BrCl under a well operating fume hood.

4.2 *Glass Wool:* Harmful if inhaled. May irritate skin. Handle with gloves.

4.3 *HCl:* Can cause severe burns. Fumes can cause severe damage to respiratory system. Flush affected areas with large amounts of water. Always work with concentrated HCl under a fume hood.

4.4 $NH_2OH{\cdot}HCl$: Harmful if inhaled or swallowed. Avoid contact with eyes and skin. Flush affected areas with water and mild soap. Has caused mutagenic effects in laboratory animals.

4.5 *Nichrome Coils:* Coils heat up to 450-500°C during a blanking cycle. Under normal room light, hot coils look no different than cold coils. Always approach coils tentatively.

4.6 $SnCl_2$: Can cause eye and skin irritation. Rinse affected areas with large amounts of water and mild soap. Persons with a history of skin disease may be at an increased risk from exposure.

4.7 *Soda-Lime:* Can cause burns. Avoid contact with skin and eyes. Rinse affected areas with large amounts of water.

4.8 *Total Mercury Standard*: Mercury in the standard can damage the nervous system. Avoid contact with skin. The working standard contains 1 to 5% BrCl.

5.0 Total Mercury Analysis Sessions

A typical total mercury analysis session often lasts from 8 to 12 hours. Depending on the number of standards, blanks, and replicates that are analyzed, 9 to 18 samples can be analyzed during one session.

Although instructions in this manual are written as linear, stepwise protocols, procedures must often be performed concurrently. Below is a suggested sequence of events for one analysis session.

5.1 Begin each analysis session by removing any mercury that may have accumulated on the six sample traps since the last analysis session. Follow the trap blanking procedure in Section 8.0. While the traps are being blanked, prepare the bubblers for blanking and analysis as prescribed in Section 8.3.

5.2 After the bubblers have been filled with an initial matrix and have started bubbling, install the soda-lime traps (Section 9.3.3) and Tenax TA® pretraps (Section 8.3.5). Note that no sample traps are attached at this time; this initial 20 minute purging serves to preclean the matrix, soda-lime and Tenax TA® pretraps. Continue the initial sample trap blanking procedure while bubbling.

5.3 After the bubblers have purged for at least 20 minutes, blank the bubblers (Section 8.4). Continue the initial sample trap blanking procedure if not already completed.

5.4 After the 20 minute purging period, analyze the gold traps from the bubbler blanks as prescribed in Section 10.0. By now the last of the sample traps should have undergone an initial blanking. Purge and trap standards to calibrate the analyzer (Section 8.4) while analyzing the bubbler blank traps. You should also prereduce the first set of three samples. (Prereduce fewer if you want to replicate analyses, of course.)

5.5 After the bubbler blank traps have been analyzed and the standards have finished purging, analyze one or two gold traps with standards. Assess the analytical and purging systems. Are the bubbler blanks low? Do the standards indicate sufficient analyzer sensitivity? If all is well, run another set of standards so trap efficiency for all traps can be assessed and also run a set of second set of bubbler blanks. If traps are behaving similarly and bubbler blanks are low and seem stable, purge and trap the prereduced samples (Section 9.2).

5.6 By this time you should have established a cycle in which one set of samples can be purged and trapped while another set is being analyzed. Continue this cycle for two to four more rounds. Don’t forget to prereduce samples a few minutes before pouring them into the bubblers.

5.7 Continue to purge and analyze samples. At minimum, a set of standards and bubbler blanks should be run midsession and at the end of an analysis session.

6.0 Protocol Organization

The stepwise protocols are organized as follows.

6.1 Step 1 - These sections describe major tasks

Caution: These sections list dangerous equipment and reagents

6.2 These sections provide detailed prescriptions on equipment use and sample manipulation.

These sections expand on the instructions given above and include precautions, reminders, and helpful tips. Background information and explanations are sometimes also included in this section.

7.0 How to Prepare the Analytical System

7.1 Step 1 - Analyzer is normally left on at all times.

7.1.1 The analyzer should be switched on at least 24 hours before beginning analyses. For a Brooks Rand Model 2 analyzer, turn on by the red rocker switch on the front panel.

Analyzer sensitivity is correlated to operating temperature. Turning the analyzer on in advance allows electronic components to warm and stabilize. If the analyzer is not switched on in advance, be certain to calibrate frequently between analyses.

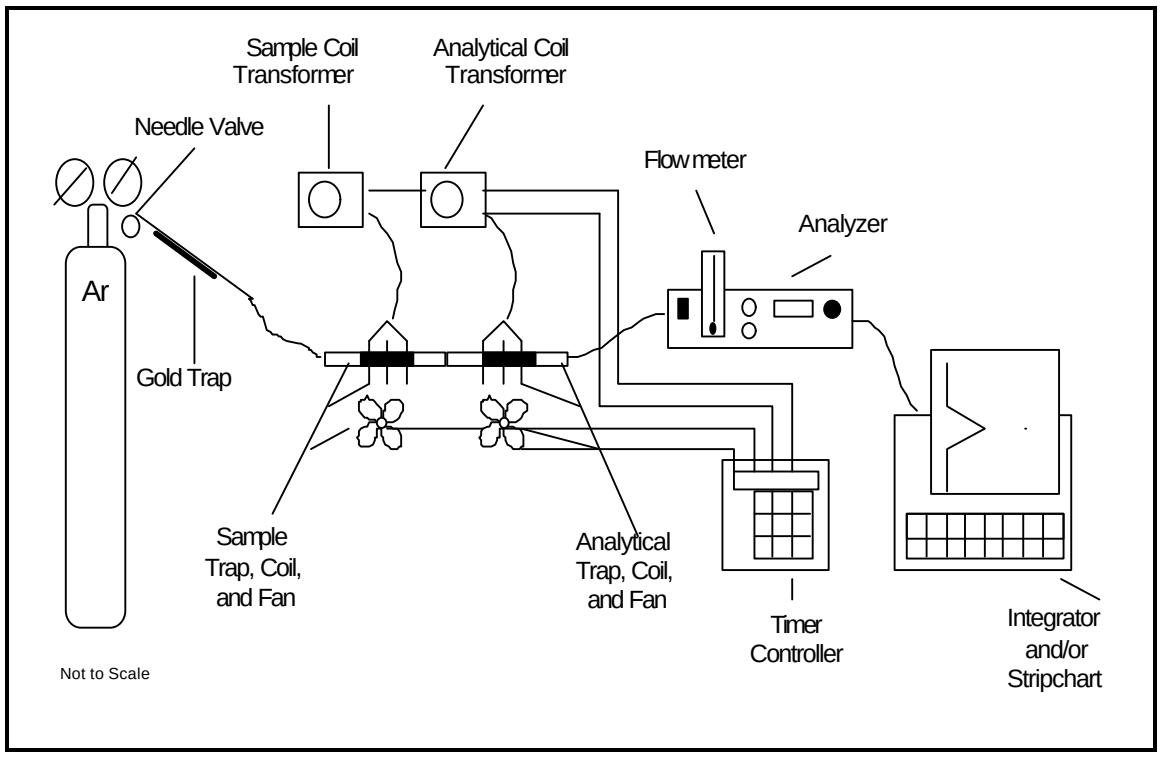

Figure 1. The Total Mercury Analytical System

7.2 Step 2 - Adjust the systems settings

7.2.1 Switch the variable transformers that power the sample and analytical nichrome coils to the 140 V position. The transformer dials should be set at approximately 10%.

These settings control the temperature ramp used to thermally desorb mercury from the gold traps. Low coil temperatures allow mercury to remain on the trap. High temperatures can compromise trapping efficiency and may vaporize the gold; which then plates out further downstream destroying tubing, fittings and the analyzer's quartz cell. If a coil emits a slight reddish glow in a dimly lighted room but does not glow under normal room light, the coil temperature is likely within the acceptable range. When in doubt, test the traps with Hg^o injections to determine efficiency and reburn the traps to assess carryover.

7.2.2 Turn on the Ar gas flow with the small needle valve feeding into the gold trap on the regulator unit. If necessary, adjust the Ar flow to about 60 units using the needle valve on the analyzer flow-meter.

The rate of Ar flow controls peak shape which should be symmetrical. If a suitable Ar flow cannot be established using the flow-meter, carefully adjust the Ar regulator valve. Adjust carefully since high pressures can cause friction connections to leak or burst.

7.2.3 Make necessary adjustments to the system settings. Consult the Appendix for appropriate total mercury analysis settings.

Some settings, such as analyzer gain, rarely need adjustment. Others, such as stripchart settings, change for various mercury species and average sample concentrations. Always check every setting before beginning analyses. Figure 1 illustrates the critical components of the analytical system.

8.0 How to Blank Traps & Bubblers and Calibrate the Analyzer

8.1 Step 1 - Blank the gold traps

8.2 *Caution*: Nichrome coils

8.2.1 Remove the end-plugs from a gold trap and orient the trap so the constriction is on the downstream or right side of the gold beads. Slip the sample nichrome coil around the trap's quartz barrel. See Figure 2.

It is important to properly orient the trap before inserting it into the coil. Twisting the trap after it is nested in the coil can break the coil or connections.

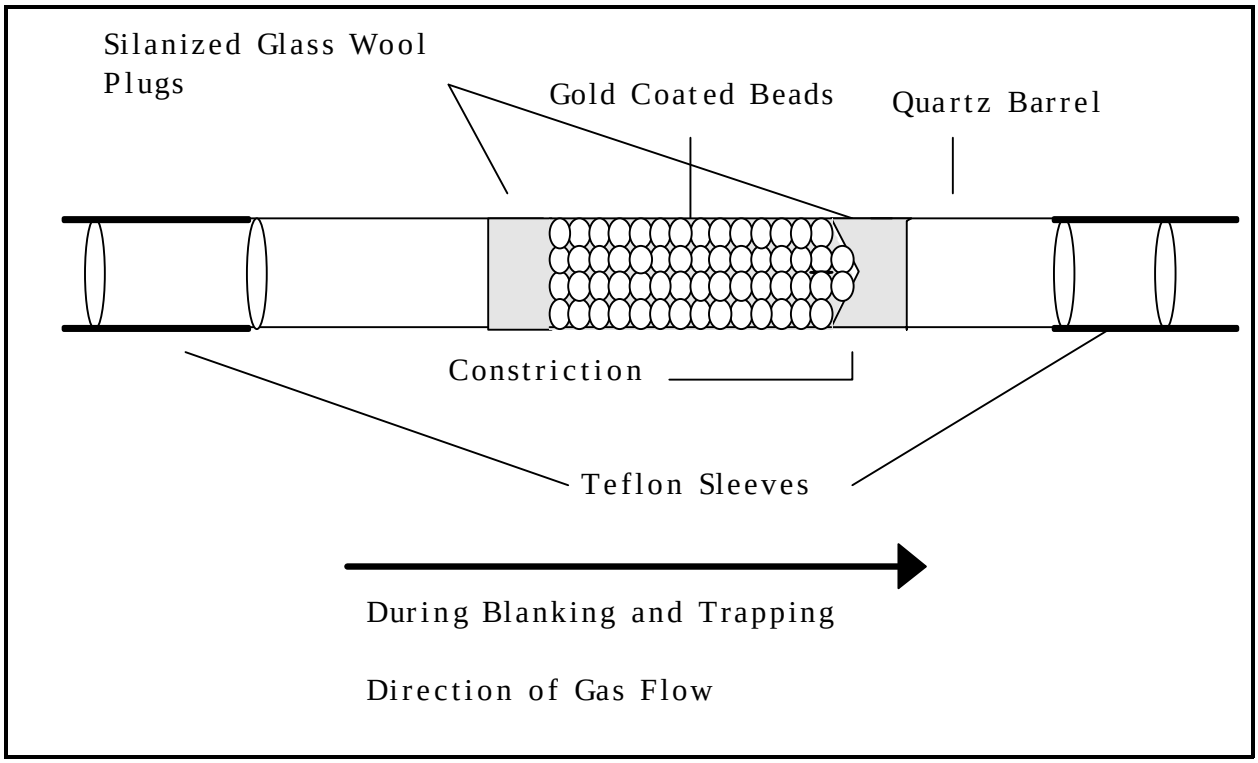

Figure 2. Gold Coated Bead Mercury Amalgamation Trap.

8.2.2 First connect the trap to the analytical (right) side of the system, then plug the Ar line into the left side of the trap.

Improperly connecting a trap to the Ar line can cause the packing material to shift or be blown out of the quartz tube.

8.2.3 Carefully adjust the position of the nichrome coils so they are centered over the gold bead region of the traps**.**

The coils should be placed in precisely the same position every time a trap is heated. Mercury can plate out on the inside of the traps barrel during normal use. This plated mercury is subsequently desorbed into the sample stream if the coil extends over a section of the trap that is not normally heated.

8.2.4 Press the sequence <PROGRAM> <1> <ON> on the timer controller.

This program switches the sample coil on for 4 minutes (Figure 3). This blanking procedure is intended only to clean residual mercury from the traps which may have accumulated since last use. Because this is not a quantitative step, the analytical trap may be purged just twice while blanking the last two traps in the set of sample traps. This will be explained in G.

8.2.5 After the 4-minute sample trap heating cycling is complete, press the sequence <CIRCUIT> <3> <ON> on the timer controller.

This switches on the sample trap cooling fan. Allow the coil and trap to cool for about 2 minutes before proceeding.

8.2.6 When the sample nichrome coil and trap are cool, press the sequence <CIRCUIT> <3> <OFF> on the timer controller. *Remove the sample gold trap; disconnect the analytical (right) side first.*

This switches off the sample trap cooling fan. Improperly disconnecting a trap from the Ar line can cause the packing material to shift or be blown out of the quartz tube.

8.2.7 Repeat Step 1 for four traps. For the last two traps, follow the above blanking procedures through C, then press the sequence <PROGRAM> <8> <ON> on the timer controller.

Program 8 appropriately controls coils and fans over an 8 minute period; both the sample and analytical traps are blanked. See Figure 3.

Figure 3. Total Mercury Analysis Event Sequence. Shaded Bars Indicate the Time Periods When Each Device Is Switched On.

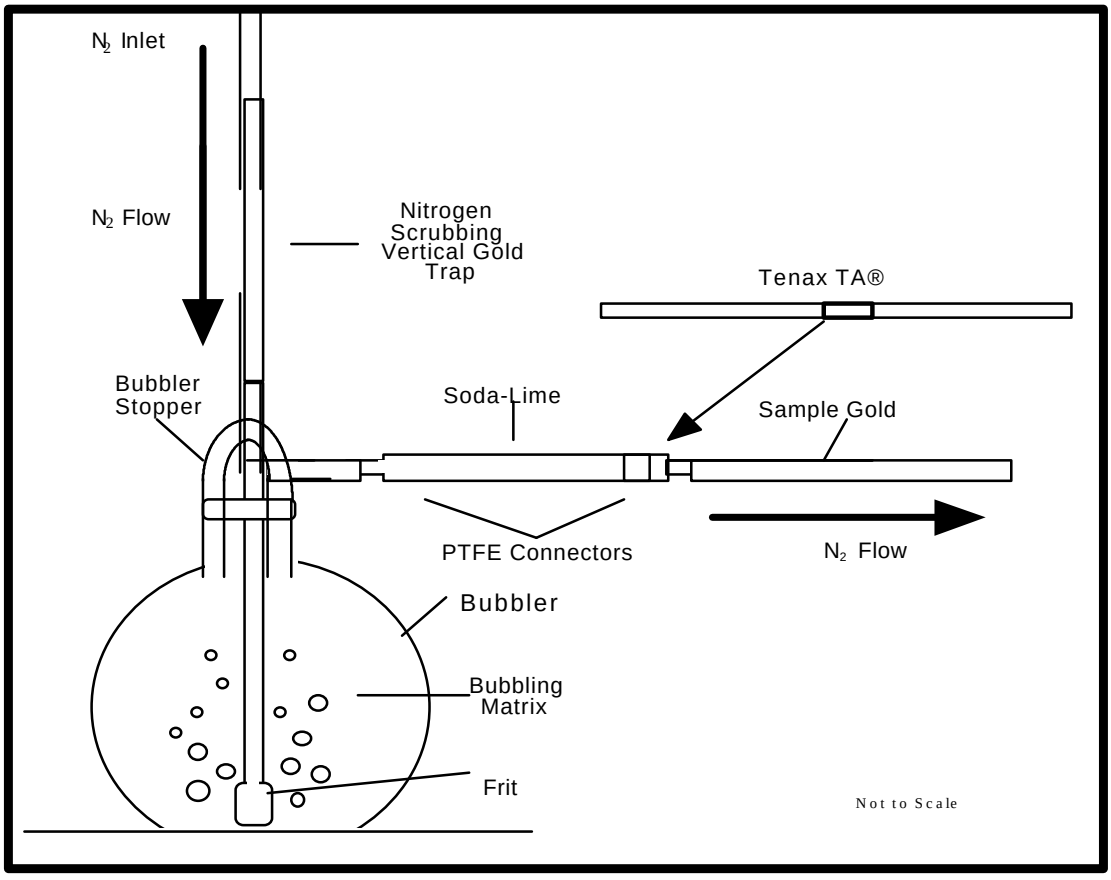

Figure 4. Total Mercury Purging and Trapping System.

8.3 Step 2 - Prepare bubblers for blanking and analyses

Caution: HCl, $SnCl_2$

8.3.1 Using clean deionized water, thoroughly rinse and partially fill each bubbler (about half full, or 125 mL).

Deionized water from a Milli-Q system is quite clean (0.1-0.3 ng/L) if the plumbing has been completely flushed.

8.3.2 Clear the HCl repipetor by pumping a few strokes into a small beaker and disposing this acid. Dispense 5 mL of clean acid into each bubbler.

Avoid producing acid fumes by filling the beaker halfway with water before pumping the repipetor.

8.3.3 Dispense 0.5 mL of $SnCl_2$ into each bubbler.

Remember to rinse the pipette tip.

8.3.4 After removing the end-plugs, attach the gold traps to the vertical inlets on the bubbler stoppers. Plug the N_2 lines into the gold traps. See Figure 4.

These gold traps scrub residual elemental mercury from the N_2. Remove the Teflon sleeve and plug from the end of the trap nearest the constriction; carefully insert the trap into the sleeve on the bubbler top. Remove just the plug from the other end of the trap and connect the N_2 line.

8.3.5 Attach soda lime traps - see Section 9.3.3 for description of soda lime traps.

8.3.6 Attach Tenax TA® pretraps (if used) downstream of the soda lime traps.
Some tributary samples, particularly early spring samples, exhibited a pronounced matrix effect which is eliminated by using these pretraps. It is recommended that the pretraps be used for all tributary samples.

8.3.7 Turn on the N_2 with the small needle valve feeding into the gold trap attached to the regulator unit. Adjust the N_2 flow into the bubblers if necessary. All flow rates should be about 50 units. See Figure 5.

The exact flow rate is unimportant. Make certain that all bubblers have approximately the same flow rate. If an appropriate N_2 flow cannot be established with the flow-meters, carefully adjust the N_2 regulator valve. Monitor the back pressure. Excessive pressure will cause the bubbler stoppers to pop off.

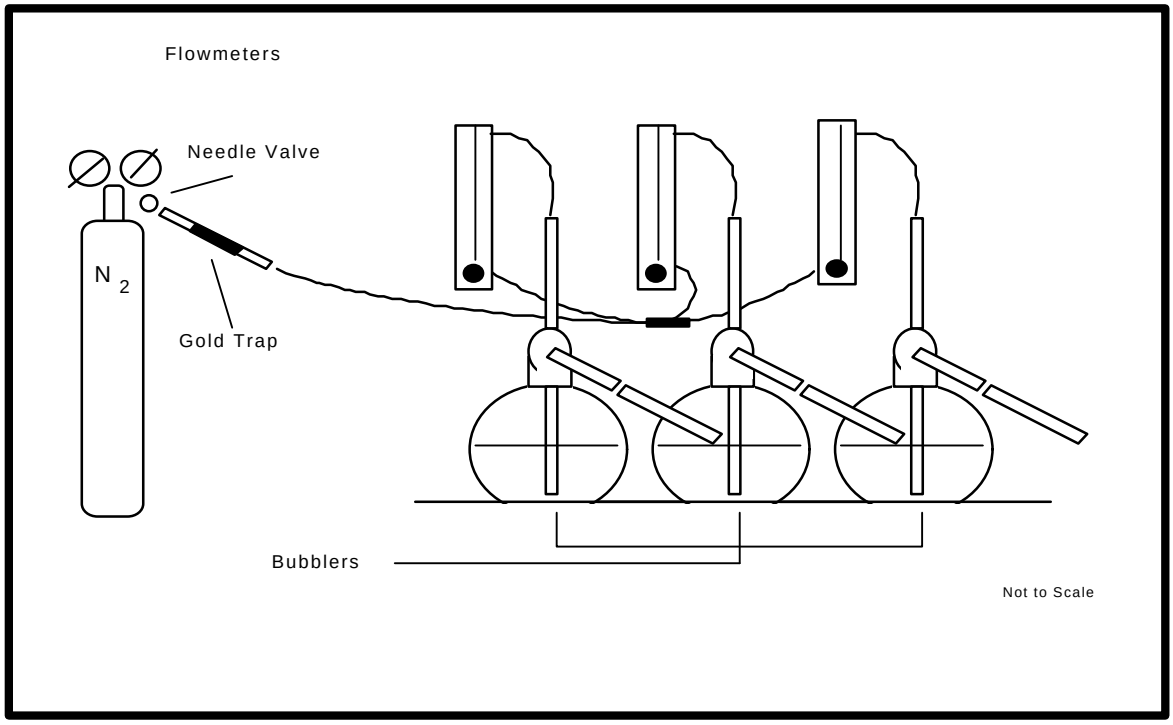

Figure 5. Total Mercury Purging and Trapping System

8.4 Step 3 - Blank the bubblers

Caution: $SnCl_2$

8.4.1 Dispense 0.5 mL of $SnCl_2$ into each bubbler containing the pre-bubbled solution from Steps 2 and 3. After removing the end-plugs, attach a gold sample trap to each Tenax TA® pretrap (if used) or directly to each soda-lime trap.

Because 0.5 mL of $SnCl_2$ is added to every sample independent of sample volume, the $SnCl_2$ is considered part of the bubbler blank. Attach the gold trap so the constriction is farthest from the Tenax TA® pretrap or soda lime trap *i.e.*, on the down-stream end.

8.4.2 Bubble for 20 minutes.

This process purges and traps the ubiquitous residual mercury from the glassware and bubbling matrix. Assume this amount of mercury is released every time a sample is purged. Because it is an artifact, this quantity of mercury must be subtracted from the standard and samples.

8.4.3 Remove and plug the sample traps; analyze each gold trap.

Turn to How to Analyze Gold Traps on Section 10.0 to continue.

8.5 Step 4 - Calibrate the Analyzer

Caution: $SnCl_2$, total mercury standard

8.5.1 Add 0.5 mL $SnCl_2$ and a series of volumes (usually 25, 50 and 100 μL) of total mercury working standard to the pre-bubbled matrix from Steps 2, 3 and 4. Attach a gold sample trap to each of the soda-lime traps connected to the bubblers.

The concentration of the total mercury working standard is 10 mg/mL; a 100 µL aliquot has 1 mg of mercury in it. If you suspect that bubbled samples will have significantly more or less mercury choose a volumes of standard that will more closely match the sample concentrations.

8.5.2 Bubble for 20 minutes.

This process purges and traps a known mass of mercury.

8.5.3 Turn off N_2; twist bubbler stopper to release seal; remove and plug the gold traps. Analyze each gold trap.

To prevent water from being sucked into the traps that scrub mercury from the N_2, always turn off the N_2 before removing the sample traps. Turn to How to Analyze Gold Traps on Section 10.0 to continue.

9.0 How to Prepare Water Samples for Analysis

9.1 Step 1 - Digest the water samples

Caution: BrCl

9.1.1 Add excess BrCl to every water sample. This will be indicated by a persistent yellow color. For tributary samples generally 5 to 8 mL per 500 mL bottle are required. Record the amount of BrCl added to the sample.

Mercury in any of its chemical forms is oxidized to Hg^{2+} by BrCl. Remember to record the amount of BrCl in each sample so the appropriate reagent blank can be subtracted.

9.1.2 Repackage sample bottles in two plastic bags. Place in a 70°C oven overnight. If the yellow color disappears, continue to add BrCl until the yellow color remains. Always wrench tighten bottles after they have been removed from the oven and cooled.

Some samples contain compounds that compete with mercury for the BrCl. These compounds effectively neutralize all the BrCl before the mercury is oxidized. For this reason, BrCl should be added in excess, indicated by a persistent yellow color. Wrench tightening is necessary, since the bottle caps become loose during the heating and cooling process.

9.2 Step 2 - Prereduce samples

Caution: $NH_2OH \cdot HCl$

9.2.1 To each digested sample, add 30 μL of $NH_2OH \cdot HCl$ solution for every 1 mL of BrCl added in Step 1. Swirl the sample.

The $NH_2OH \cdot HCl$ reduces (*i.e*. neutralizes) the excess BrCl in the sample.

9.2.2 Allow the sample to react for 5 minutes.

The yellow color from the excess BrCl should disappear.

9.3 Step 3 - Purge samples and capture mercury on gold traps

Caution: $SnCl_2$

9.3.1 Place a bubbler on a pan balance and tare. The bubbler may be empty or contain a purged solution from bubbler blanks, standards or a previous sample. Dispense about 100 to 125 mL of sample into the bubbler. Try to keep the same overall volume in the bubbler during the day. Record the exact volume dispensed.

Because the matrix from the blanks, standards and bubbled samples has been purged of mercury, sometimes it is more efficient to simply add another sample without emptying the bubbler. Make sure, however, that the new sample will fit into the bubbler before pouring. Of course the volume of sample dispensed into the bubbler can be more or less than prescribed here, depending on the suspected mercury concentration. By keeping the bubbled volume within a 1 mL range for an entire analysis session, you can facilitate easy concentration calculations. Also, by keeping the same overall liquid level in the bubbler constant you minimize the possibility of cleaning bubbler surfaces not cleaned initially at the beginning of the day.

9.3.2 Add 0.5 mL of $SnCl_2$ to the sample and cap.

The $SnCl_2$ reduces the Hg^{2+} in the sample to Hg^0. Hg^0 is volatile and can be purged from the water sample onto gold traps.

9.3.3 Attach a gold sample trap to each soda-lime trap or Tenax TA ® pretrap. Reconnect the N_2 lines.

Attach the gold trap so the constriction is farthest from the soda lime or Tenax TA® pretrap, *i.e,*. on the down-stream end.

9.3.4 Bubble for 20 minutes.

This process purges mercury from the sample water; the mercury is trapped on the gold coated beads.

9.3.5 Turn off N_2, twist bubbler stoppers to release seal; remove and plug the sample traps. Analyze each gold trap.

To prevent water from being sucked into the vertical gold traps that scrub mercury from the N_2, always disconnect the N_2 lines before removing the sample traps. Turn to How to Analyze Gold Traps on Section 10.0 to continue

10.0 How to Analyze Gold Traps

10.1 *Caution*: Nichrome coils

10.1.1 Remove the end-plugs from a gold trap and orient the trap so the constriction is on the downstream or right side of the gold beads. Slip the nichrome coil around the trap's quartz barrel.

It is important to properly orient the trap before inserting it into the coil. Twisting the trap after it is nested in the coil can break the coil or connections.

10.1.2 First connect the trap to the analytical (right) side of the system, then plug the Ar line into the left end of the trap

Improperly connecting a trap to the Ar line can cause the packing material to shift or be blown out of the quartz tube.

10.1.3 Carefully adjust the position of the nichrome coils so they are centered over the gold bead region of the traps.

The coils should be placed in precisely the same position every time a trap is heated. Mercury can plate out on the inside of the traps barrel during normal use. This plated mercury is subsequently desorbed into the sample stream if the coil extends over a section of the trap that is not normally heated.

10.1.4 Press the sequence <Program> <8> <ON> on the timer controller. If you are using an integrator.

Program 8 appropriately controls coils and fans over an 8 minute period; both the sample and analytical traps are heated. See Figure 3.

10.1.5 When the cooling fans turn off (after about 8 minutes), write the sample identification next to the peak on the chart or integrator paper. Remove the sample gold trap; disconnect the analytical (right) side first.

Improperly disconnecting a trap from the Ar line can cause the packing material to shift or be blown out of the quartz tube.

10.1.6 Repeat Step 1 for the other two traps.

With a system of three bubblers, sample bubbling time is approximately equal to the time needed to analyze three traps. Establish a cycle where one set of three traps is being analyzed while the other set is capturing purged mercury.

11.0 How to Prepare Soda Lime Traps

11.1 *Caution*: Glass wool, soda-lime

11.1.1 Assemble materials on the lab bench before beginning. You'll need FEP tubes, PTFE machined connectors (10 mM to 5 mM), glass wool, teflon tape and soda-lime.

The FEP tubes and PTFE connectors can be used more than once between cleanings. Repack the traps with fresh soda-lime at least every other day of analysis.

11.1.2 Create six small balls of glass wool to plug the ends of the traps.

The balls of glass wool should be about 0.5 cm in diameter. They need not be very dense.

11.1.3 Place one of the glass wool balls into an FEP tube. Carefully wrap a piece of teflon tape around a machined connector. Make sure the tape is free of wrinkles, as this can be a conduit for leaks, and is not covering the bore hole for gas flow. Insert this machined connector carefully so the teflon tape is not bunched or wrinkled.

The connector should fit tightly in the tube. Take care not to pinch an excess of glass wool fibers between the outside of the connector and the inside of the tube. This can create also leaky connections.

11.1.4 Holding the connector, scoop soda-lime into the tube. Fill the tube to 0.25 cm of the unplugged end.

To avoid spilling soda-lime around the Clean Lab, stand over a trash can while filling the traps.

11.1.5 Place another glass wool plug into the tube and insert a connector wrapped with teflon tape. Wipe any soda-lime dust off the outside of the trap with a towel.

Both the soda-lime and the glass wool will compress to allow insertion of the connector.

11.1.6 After building 2 more traps, place one trap on the horizontal outlet of each bubbler.

The soda-lime traps are symmetrical so orientation is not important.

11.1.7 After the soda-lime traps have been installed, bubble overnight in a MilliQ matrix with mL HCl and a few mL $SnCl_2$ at a flow rate of 5 to 10 units.

This process cleans mercury from the soda-lime traps and the matrix in the bubblers.

Note: Soda lime may be reused once. After the first use, dry the traps by attaching directly to N_2 pretraps overnight applying a N_2 flow rate of about 5 units

12.0 How to Prepare Reagents

12.1 Stannous Chloride

To prepare the stannous chloride solution, 200 g of $SnCl_2$ is measured using a large weighing boat and Teflon spatula. The crystals are poured into a clean 1 L Teflon bottle and then 100 mL of concentrated Tracepure HCl is added to the 1 L bottle with the $SnCl_2$ crystals. This can be done either using the HCl repipetor or a type of clean volumetric glassware. Milli-Q water is then added to bring the solution to 1 L. The solution is purged with N_2 overnight and then labeled $SnCl_2$ and the date the solution was purged. The $SnCl_2$ solution is stored doubled-bagged in the refrigerator.

12.2 Hydroxylamine Hydrochloride

To prepare $NH_2OH{\cdot}HCl$ solution, 300 g of $NH_2OH{\cdot}HCl$ crystals are measured using a large weighing boat and Teflon spatula. The crystals are poured into a clean Teflon 1 L bottle and then filled to 1L with Milli-Q water. (To make 125 mL of solution use 37.5 g of $NH_2OH{\cdot}HCl$ crystals and 125 mL bottle.) Cap the bottle and shake until all crystals are dissolved. For each 1 L of solution, add 1 mL of $SnCl_2$ and purge the solution overnight with N_2.

12.3 Bromine Monochloride

Caution: To prepare BrCl solution, all work must be done in the fume hood and wearing safety goggles.

First 8.6 g of KBr is measured in the hood using a weighing boat and Teflon spatula. The KBr is poured in the 1L Teflon bottle (BrCl stock solution bottle) and the bottle is then filled with 800 mL of concentrated Tracepure HCl and a clean magnetic stir bar added. For approximately an hour the solution is stirred in the fume hood with a stir plate. After the hour is up, *very slowly* add the $KBrO_4$ crystals while stirring slowly. Add small amounts of crystals and only add more when fizzing has stopped. Then allow the solution to stir with the cap on loosely for another hour. Smaller amounts of this stock solution (about 50 mL) are purified in a teflon, sub-boiling distillation apparatus (Savillex®).

12.4 Mercury Standards

To prepare the mercury secondary standard use a stock mercury standard of 1000 mg/L. In a clean 100.0 mL class A volumetric flask, pipette 100.0 μL of the stock solution and 5 mL of BrCl solution into the volumetric flask and dilute to 100.0 mL with Milli-Q water. This pipetting must be done extremely accurately and should be redone if pipette error or contamination occurs. After mixing, the solution is poured into a clean 125 mL Teflon bottle and labeled with Hg 2, ID of stock solution, the date, and your initials. This can be stored in a refrigerator for up to one year. To prepare the working standard, dispense 1.00 mL of the mercury secondary standard and 1 to 5 mL of BrCl solution into another clean 100 mL class A volumetric flask and bring to volume with

MilliQ water. This pipetting must also be done with great accuracy. After mixing the solution, pour it into a clean 125 mL Teflon bottle and label with Hg Working Standard, the date, and your initials. This solution should be replaced monthly.